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(21) International Application Number: PCT/US97/07789 (22) International Filing Date: 6 May 1997 (06.05.97) (30) Priority Data: 08/650,920 16 May 1996 (16.05.96) US (71) Applicant: NAPP SYSTEMS, INC. [US/US]; 360 South Pacific, San Marcos, CA 92069 (US). (72) Inventors: MUELLER, Gregory, E.; 1721 Red Barn Road, Encinitas, CA 92024 (US). MALE, Mitch, G.; 3609 Grand Avenue, San Marcos, CA 92069 (US). ROBERTS, David, H.; 2704 Levante Street, Carlsbad, CA 92009 (US). (74) Agent: REITER, Stephen, E.; Gray, Cary, Ware & Freidenrich, Suite 1600, 4365 Executive Drive, San Diego, CA 92121 (US).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHODS TO INCREASE THE EXPOSURE SENSITIVITY OF PHOTOPOLYMERIZABLE MATRICES AND APPARATUS USEFUL THEREFOR (57) Abstract In accordance with the present invention, there are provided methods to substantially increase the effective exposure sensitivity of photopolymerizable materials without chemical modification thereof. This is accomplished by subjecting such materials to a relatively low energy pre-exposure prior to subjecting such materials to the main imaging exposure. Increase in the effective exposure sensitivity of photopolymerizable materials provides improved image quality in the exposed matrix and allows increased exposure speeds to be employed. In accordance with another aspect of the present invention, there are provided imaging apparatus useful for carrying out the above-described process. Invention apparatus enable one to increase the effective exposure sensitivity of photopolymerizable materials.		

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Methods to Increase the Exposure Sensitivity
of Photopolymerizable Matrices and
Apparatus Useful Therefor

FIELD OF THE INVENTION

The present invention relates to methods for the treatment of photopolymerizable matrices (e.g., printing plates) and related materials to impart an image thereon.

5 In a particular aspect, the present invention relates to apparatus useful for imparting an image onto photopolymerizable matrices and related materials.

BACKGROUND OF THE INVENTION

Images can be imparted to photosensitive polymeric materials (e.g., materials employed for the production of printing plates) in a variety of ways. For example, a mask (typically a negative) can be placed over the matrix, which is then exposed to light of sufficient energy to promote the crosslinking of the matrix. This

10 crosslinking occurs only where light is allowed to impact the matrix. Uncured photosensitive polymeric material is then removed (e.g., by washing), leaving the desired image.

With the advent of laser technology, it is now possible to directly impart an image to a photosensitive matrix without the need for a mask. Instead, coherent energy can be directed onto the surface of the photosensitive matrix in the desired pattern. However, when employing coherent energy to expose a photosensitive matrix, the available power is relatively low and

20 expensive, and exposure times are typically quite short. To address these problems, the use of highly sensitive and reactive resins is required, so that the imaged matrix avoids the problems associated with insufficient curing (e.g., lack of resin strength, poor resilience, solvent

25 swell (due to the generation of inadequate molecular

30

weights during the curing process), and the need for extended exposure times).

To address these problems, efforts have been made to develop more highly reactive photosensitive resins. Such materials would be expected to give more complete crosslinking, even with brief laser exposure, as the desired image is scanned onto the resin. Alternatively, conventional photosensitive resins may find wider use in the field of laser imaging if methods can be developed to enhance the exposure sensitivity of such materials. Furthermore, there is a clear need in the art for photopolymerization reactions to proceed as rapidly as possible, thereby allowing for the rapid conversion of photopolymerizable materials into finished articles.

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BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, we have discovered that a substantial increase in the effective exposure sensitivity of photopolymerizable materials can be achieved by subjecting such materials to a relatively low energy pre-exposure prior to subjecting such materials to the main imaging exposure. Increase in the effective exposure sensitivity of photopolymerizable materials provides improved image quality (e.g., resolution of fine detail) in the exposed matrix and allows increased exposure speeds to be employed.

In accordance with another aspect of the present invention, there are provided imaging apparatus useful for carrying out the above-described process. Invention imaging apparatus enable one to increase the effective exposure sensitivity of photopolymerizable materials.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are provided methods to increase the effective exposure sensitivity of a photopolymerizable matrix when digitally
5 imaged. The invention method comprises pre-exposing the above-described matrix (i.e., subjecting the matrix to a low fluence of actinic radiation) prior to digitally imaging the matrix.

Thus, according to the present invention, the
10 effective exposure sensitivity of a photopolymerizable material is substantially increased. In other words, without any chemical modification of the photopolymerizable material, the energy input required to cause photopolymerization thereof is reduced.

As is commonly used in the art, the term "actinic
15 radiation" refers to electromagnetic radiation capable of initiating photochemical reactions. Ultraviolet and visible wavelength radiation (with wavelengths typically falling in the range of 300-700 nm) is commonly employed
20 for this purpose. Preferred wavelengths are those which correspond to the spectral sensitivity of the photopolymerizable material being imaged.

As employed herein, "pre-exposure" (i.e.,
"exposure to a low fluence of actinic radiation") refers to
25 radiation which imparts less energy to the photopolymerizable matrix than the threshold level required to initiate a substantial level of curing thereof. The "threshold level" required to initiate a substantial level of curing of the photopolymerizable matrix can vary widely,
30 depending on such factors as the particular material being imaged, the processing methodology employed for developing the imaged material, and the like. Radiation levels are said to exceed threshold levels when the pre-exposed

photopolymer cannot be completely removed from the support therefor under normal processing conditions.

Thus, while some level of curing of the photopolymerizable matrix may be induced by pre-exposure (i.e., by exposure to a low fluence of actinic radiation), the level of curing of the photopolymerizable matrix imparted by this treatment is generally controlled so as to be insufficient to produce any significant change in the physical properties of the photopolymerizable matrix.

Pre-exposure contemplated by the present invention can be imparted either by coherent or non-coherent radiation, and will typically have a wavelength comparable to the wavelength employed for the actual imaging exposure. A variety of methods can be used to achieve the desired pre-exposure employed herein. For example, a lower intensity of radiation than used for the imaging exposure can be employed, or a longer wavelength than used for the imaging exposure can be employed, etc.

Typically, pre-exposure employed in the practice of the present invention is accomplished employing radiation which imparts energy equal to about 10-99 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix. Preferably, pre-exposure employed in the practice of the present invention is accomplished employing radiation which imparts energy equal to about 75-96 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix, with radiation which imparts energy equal to about 80-90 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix being presently preferred.

In accordance with the present invention, the area of photopolymerizable matrix subjected to pre-exposure

(at any particular point in time) is at least as great as the area of the same portion of the matrix as is subjected to digital imaging substantially immediately following the pre-exposure. It is presently preferred that over the entire surface of the photopolymerizable matrix, there is a substantially constant delay between initial pre-exposure of photopolymerizable matrix and the imaging exposure which follows. Typically, photopolymerizable matrix is subjected to pre-exposure at least about 0.05 seconds before, but no greater than about 5 minutes before being subjected to digital imaging. Preferably, the photopolymerizable matrix is subjected to pre-exposure at least about 0.1 seconds, but no greater than about 30 seconds before being subjected to digital imaging.

Photopolymerizable matrices contemplated for use in the practice of the present invention include flexographic printing plates, letterpress printing plates, offset printing plates, circuit board resists, stereolithography resins, and the like. Such materials can be prepared from a variety of photopolymerizable resins, such as, for example, (meth)acrylate-based resins (see, for example, U.S. Patent No. 5,348,844, incorporated herein by reference), thiol/ene-based resins (see, for example, U.S. Patent No. 3,783,152, incorporated herein by reference), vinyl ether-based resins (see, for example, U.S. Patent No. 5,446,073, incorporated herein by reference), cationic-based resins (see, for example, U.S. Patent No. 5,437,964, incorporated herein by reference), diazonium-based resins (see, for example, U.S. Patent No. 4,263,392, incorporated herein by reference), and the like, as well as combinations of any two or more thereof.

Digital imaging contemplated by the present invention is typically accomplished by exposure of the photopolymerizable matrix to coherent (e.g., laser) irradiation.

As readily recognized by those of skill in the art, the angle of incidence at which the photopolymerizable matrix is contacted with either the pre-exposure radiation and/or the digital imaging radiation can vary substantially. For example, with relatively thin photopolymer matrices (i.e., thicknesses of about 2 microns or less), the angle of incidence is relatively unimportant (and consequently can vary widely, e.g., from 0° up to about 45° or more). Similarly, photopolymerizable matrices used for the preparation of circuit boards (i.e., having thicknesses in the range of about 1-2.5 mils), are relatively insensitive to the angle of incidence. In contrast, thicker photopolymer matrices (i.e., thicknesses of greater than about 5 mils) are typically less tolerant of the angle of incidence, and consequently will vary within a narrower range than set forth above, e.g., from 0° up to about 15°. Indeed, it is presently preferred that the angle of incidence be substantially perpendicular to the photopolymerizable matrix (i.e., an angle of incidence of about 0°), in order to maximize penetration of the incident radiation into the photopolymerizable matrix, thereby maximizing the effectiveness of the pre-exposure and/or digital imaging.

In accordance with another embodiment of the present invention, there are provided improved imaging apparatus for digitally imaging photopolymerizable surfaces. Invention apparatus comprises conventional imaging equipment (having a first exposure means for digitally imaging the photopolymerizable surface), modified so as to include a second exposure means capable of delivering pre-exposure radiation to the photopolymerizable surface substantially immediately prior to digital imaging thereof.

As employed herein, "exposure means" refers to both a source of radiation, as well as the resulting beam

produced by said source. When reference is made herein to specifically directing the output of an exposure means, it is understood that it is the beam produced by the exposure means which is actually being directed.

5 Imaging apparatus contemplated for use in accordance with the present invention include any configuration typically used for exposure of a photopolymerizable matrix to impart an image thereto. Such apparatus include exterior-drum devices (see, for example, 10 European Patent Application No. 491,368, U.S. Patent No. 5,247,883 and U.S. Patent No. 5,385,092, each of which are hereby incorporated by reference herein); flatbed devices (see, for example, U.S. Patent No. 5,385,092 and U.S. Patent No. 4,312,590, each of which are hereby incorporated 15 by reference herein); interior-arc devices (also known as internal drum devices; see, for example, U.S. Patent No. 5,385,092 and U.S. Patent No. 4,054,928, each of which are hereby incorporated by reference herein); and the like.

 Pre-exposure contemplated by the present 20 invention can be accomplished employing either coherent or non-coherent radiation, and can be provided by a variety of sources, e.g., an ion gas laser (e.g., an argon ion laser, a krypton laser, a helium:cadmium laser, and the like), a solid state laser (e.g., a frequency-doubled Nd:YAG laser), 25 a semiconductor diode laser, an arc lamp (e.g., a medium pressure mercury lamp, a Xenon lamp, a carbon arc lamp, and the like), and the like. Exposure sources capable of providing ultraviolet and visible wavelength radiation (with wavelengths typically falling in the range of 300-700 30 nm) are commonly employed for the practice of the present invention. Preferred wavelengths are those which correspond to the spectral sensitivity of the photopolymerizable material being imaged.

Those of skill in the art recognize that the first exposure means and the second exposure means can be provided by a single source, or by two separate elements. When a single source is employed (in conjunction with a beam splitter), a portion of the beam is employed for pre-exposure of the photopolymerizable matrix, and the remainder of the beam is employed as the main exposure beam.

In accordance with yet another embodiment of the present invention, there are provided apparatus comprising:

support means for a photopolymerizable matrix, a first exposure means capable of delivering pre-exposure radiation to the surface of said photopolymerizable matrix, wherein said first exposure means is movably positioned with respect to said support means, and

a second exposure means capable of digitally imaging said matrix, wherein said second exposure means is movably positioned with respect to said support means, and wherein the positioning of said first exposure means and said second exposure means are interrelated so as to effect a substantially constant delay between pre-exposure of a photopolymerizable matrix mounted on said support means and said digital imaging.

Support means contemplated for use in the practice of the present invention include any means suitable to aid in presenting the photopolymerizable matrix to the pre-exposure and the imaging exposure contemplated herein. Examples include the support carriage of an exterior-drum device, the support element of a flatbed device, the support element of an interior-arc device, and the like.

In accordance with the present invention, the means capable of delivering pre-exposure radiation can

deliver either coherent or non-coherent radiation. Such radiation will impart less energy to the photopolymerizable matrix than the threshold level required to initiate substantial curing of the photopolymerizable matrix. As
5 noted above, pre-exposure contemplated by the present invention can be provided by a separate source, or by the same source as used to generate the main exposure beam.

Apparatus according to the invention is designed so that the area of photopolymerizable matrix subjected at
10 any particular point in time to pre-exposure by said first exposure means is at least as great as the area of the same portion of the matrix as is later subjected to exposure by the second exposure means (typically substantially immediately following pre-exposure).

15 In order to scan extensive portions of the photopolymerizable matrix, it must be possible for the image to be imparted to the photopolymerizable matrix (i.e., the support means) to be movably positionable with respect to the output beam of said first and second
20 exposure means. Thus, in one aspect of the invention, the support means is movably adjustable with respect to the output beam of said first and second exposure means. In another aspect of the invention, the output beam of said first and second exposure means are movably adjustable with
25 respect to a relatively stationary support means. In yet another aspect of the invention, both the support means and the output beam of said first and second exposure means are movably adjustable with respect to one another.

The invention will now be described in greater
30 detail by reference to the following non-limiting examples.

Example

The effect of pre-exposure according to the invention on exposure sensitivity of a variety of photopolymerizable resins was tested as follows. Three
5 different commercially available resins were tested:

NAPPflex NF-1 (NAPP Systems Inc., San Marcos, CA),

Printight EM76 (Toyobo Co., Ltd. Osaka, Japan),

Anocoil 372 (Anocoil, Rockville, CT 06066).

10 Plates were exposed employing an external drum device and an ultraviolet argon ion laser delivering wavelengths in the range of 333-364 nm (although wavelengths falling in the range of about 320-550 nm, with wavelengths in the range of about 330-365 nm are also
15 suitable). The power for pre-exposure was split from the main beam using a beamsplitter, and injected into a fiber optic which guided the beam to the appropriate point. The time delay between the pre-exposure and main beams typically falls in the range of about 30 sec.

20 Each of the test materials was subjected to the following procedure: First, the pre-exposure threshold fluence was determined by subjecting the material under test to a series of pre-exposures of varying intensities; the material under test was then processed according to the
25 manufacturer's instructions. The threshold fluence is defined as the fluence required to produce a slight scum on the plate after processing (the pre-exposure threshold fluence was thus determined to within a few percent). Second, the material under test was exposed to the desired
30 pre-exposure, and then a brief (e.g., 5 millisecond) exposure to irradiation by the main laser. The plate was then processed according to the manufacturer's instructions and evaluated. The evaluation comprised measuring the radius, r , of the polymerized area left by the main

exposure with a measuring microscope and finding the main imaging threshold fluence, $I(r)$, using the following equation:

$$I(r) = I_0 \exp(-2(r/w)^2)$$

5 wherein I_0 is the peak fluence, and w is $1/e^2$ beam radius.

Each of the photopolymerizable resins was subjected to pre-exposure fluences of 0%, 25%, 50% and 90% of the pre-exposure threshold fluence, followed by the appropriate imaging fluence, then processed as per
10 manufacturer's specifications. Results are summarized in the following table.

Table

Material	Peak Main Exposure Fluence	Pre-Exposure		Imaging Fluence (mJ/cm ²)
		Approx. % Threshold	Fluence (mJ/cm ²)	
NAPPflex NF-1	331 mJ/cm ²	0	0	20.6
		25	4.0	15.4
		50	8.0	12.6
		90	14.3	3.4
Anocoil 372	199 mJ/cm ²	0	0	112.9
		25	19.8	98.9
		50	39.3	60.9
		90	70.8	35.7
Printight (EM76)	83 mJ/cm ²	0	0	17.4
		25	2.5	13.9
		50	4.9	7.9
		90	8.8	1.5

Inspection of the results presented in the table indicates that, for each material tested, an increase in pre-exposure fluence results in a decrease of the imaging

fluence. This reflects an increase in the effective sensitivity of the test material to actinic radiation.

In addition, in most instances, the total power requirement (i.e., the total of the power requirement for the pre-exposure and imaging exposures) is reduced by the invention process employing a low fluence pre-exposure, followed by an imaging exposure.

While the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that modifications and variations are within the spirit and scope of that which is described and claimed.

That which is claimed is:

1. A method to increase the effective exposure sensitivity of a photopolymerizable matrix when digitally imaged, said method comprising pre-exposing said matrix to a low fluence of actinic radiation prior to digitally
5 imaging said matrix.

2. A method according to claim 1 wherein said digital imaging is accomplished by exposure of said photopolymerizable matrix to laser irradiation.

3. A method according to claim 1 wherein said photopolymerizable matrix is selected from a flexographic printing plate, a letterpress printing plate, an offset printing plate, a circuit board resist, or a
5 stereolithography resin.

4. A method according to claim 1 wherein said photopolymerizable matrix is selected from (meth)acrylate-based resins, thiol/ene-based resins, vinyl ether-based resins, maleate/fumarate-based resins, cationic-based
5 resins, naphthalene diazoquinone-based resins, or mixtures of any two or more thereof.

5. A method according to claim 1 wherein said pre-exposure is accomplished employing radiation which imparts less energy to said matrix than the threshold level required to initiate a substantial level of curing of the
5 photopolymerizable matrix.

6. A method according to claim 5 wherein the level of curing of the photopolymerizable matrix is not sufficient to produce any significant change on the physical properties of the photopolymerizable matrix.

7. A method according to claim 1 wherein said pre-exposure is accomplished employing radiation which imparts energy equal to about 10-99 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix.

8. A method according to claim 1 wherein said pre-exposure is accomplished employing radiation which imparts energy equal to about 75-96 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix.

9. A method according to claim 1 wherein said pre-exposure is accomplished employing radiation which imparts energy equal to about 80-90 % of the threshold level required to initiate substantial curing of the photopolymerizable matrix.

10. A method according to claim 5 wherein said radiation is coherent.

11. A method according to claim 5 wherein said radiation is non-coherent.

12. A method according to claim 1 wherein the area of said matrix subjected to pre-exposure at any particular point in time is at least as great as the area of the same portion of said matrix as is subjected to digital imaging immediately following said pre-exposure.

13. A method according to claim 12 wherein said matrix is pre-exposed at least 0.05 seconds before being subjected to digital imaging, but no greater than about 5 minutes before being subjected to digital imaging.

14. A method according to claim 12 wherein said matrix is pre-exposed at least 0.1 seconds before being subjected to digital imaging, but no greater than about 30 seconds before being subjected to digital imaging.

15. A method according to claim 12 wherein, over the entire surface of said photopolymerizable matrix, there is a substantially constant delay between pre-exposure of said photopolymerizable matrix and said digital imaging.

16. A method according to claim 2 wherein said photopolymerizable matrix is contacted with said pre-exposure radiation and said laser radiation at an angle of incidence of up to about 45°.

17. A method according to claim 16 wherein said angle of incidence is about 0°C, i.e., the angle of incidence is substantially perpendicular to said photopolymerizable matrix.

18. In an imaging apparatus for digitally imaging a photopolymerizable surface, the improvement comprising including in said apparatus a second exposure means capable of pre-exposing the photopolymerizable surface substantially immediately prior to digital imaging thereof.

19. An apparatus according to claim 18 wherein said photopolymerizable surface is selected from a flexographic printing plate, a letterpress printing plate, an offset printing plate, a circuit board resist, or a stereolithography resin.

20. An apparatus according to claim 18 wherein said imaging apparatus is selected from an exterior-drum device, a flatbed device or an interior-arc device.

21. Apparatus comprising:
support means for a photopolymerizable matrix,
a first exposure means capable of pre-exposing
the surface of said photopolymerizable matrix, wherein said
5 first exposure means is movably positioned with respect to
said support means, and
a second exposure means capable of digitally
imaging said matrix, wherein said second exposure means is
movably positioned with respect to said support means, and
10 wherein the positioning of said first exposure means and
said second exposure means are interrelated so as to effect
a substantially constant delay between pre-exposure of a
photopolymerizable matrix mounted on said support means and
said digital imaging.
22. Apparatus according to claim 21 wherein said
support means is selected from an exterior-drum device, a
flatbed device or an interior-arc device.
23. Apparatus according to claim 21 wherein said
means capable of delivering pre-exposure radiation imparts
less energy to said matrix than the threshold level
required to initiate substantial curing of the
5 photopolymerizable matrix.
24. Apparatus according to claim 21 wherein the
area of said matrix subjected at any particular point in
time to exposure by said first exposure means is at least
as great as the area of the same portion of said matrix as
5 is subjected to exposure by said second exposure means
substantially immediately following said pre-exposure.
25. Apparatus according to claim 21 wherein said
support means is movably adjustable with respect to said
first and second exposure means.

26. Apparatus according to claim 21 wherein said first and second exposure means are movably adjustable with respect to said support means.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07789

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G03F 7/20, 7/22

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/281.1; 280.1; 300,302,306,327,945,269,190,311,285.1, 286.1; 264/401; 101/471,463.1; 425/174.4; 347/262,264

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,910,121 A (RIEDIKER et al) 20 March 1990, column 1, lines 34-44, column 7, lines 26-44, column 8, lines 13-38, column 10, lines 3-23, 54-68, column 11, lines 1-6, Example 42.	1-20
Y	US 3,144,331 A (THOMMES) 11 August 1964, column 1, lines 19-46, 62-72; column 2, lines 1-19; column 3, lines 5-33; column 11, lines 36-53.	1-20
Y	US 5,330,882 A (KAWAGUCHI et al) 19 July 1994, column 1, line 11 to column 2, line 11; column 4, line 25 to column 5, line 5, column 5, lines 27-62.	1-6, 10-20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	CA 2,101,582 A1 (HOECHST AKTIENGESELLSCHAFT) 06 February 1994, page 1, lines 12-30, page 3, lines 7-14, page 4, line 34 to page 6, line 32, claims and Figure 2.	1-3, 5-26 — 1-26
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X	US 4,945,032 A (MURPHY et al) 31 July 1990, abstract, column 2, lines 59 - column 4, lines 68, examples, claims.	1-12, 15-20 — 1-12, 15-20
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X	E. J. Murphy et al, Radiation Curing, February/May 1989, pages 3-7.	1-12, 15-20 — 1-12, 15-20
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X	US 5,236,812 A (VASSILIOU et al) 17 August 1993, Figures 1, 4, 5, column 4, lines 19-51, column 6 lines 49 - column 7, lines 68, column 8, lines 64 - column 10, lines 31, column 15, lines 43 - column 23, lines 7, claim 1.	1-26 — 1-26
Y	US 5,104,592 A (HULL et al) 14 April 1992, column 27, lines 11-28.	1-26
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Y	US 4,609,615 A (YAMASHITA et al) 02 September 1986, column 2, lines 13-23, column 5, lines 32-45, Example 16, claim 4.	1-4, 12
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,544,627 A (TAKAHASHI et al) 01 October 1985, column 22, lines 12- column 23, lines 42, Examples.	1 - 12
Y		18 - 20
Y	SU 595694 A (NIKOLSKII V G) 28 February 1978, English Abstract.	3
Y	GB 1,136,544 A (GEVAERT-AGFA N.V.) 11 December 1968, page 1, lines 13-79, Examples.	4
Y	KULAK, J.E. et al. Tool for blanket exposure of photopolymer films, IBM Technical Disclosure Bulletin, December 1975. Vol. 18. No. 7. page 2179.	18-26
Y	US 3,832,421 A (MORGAN) 27 August 1974, column 12, lines 4-68, column 10, lines 36-68.	1-4
Y	US 4,410,562 A (NEMOTO et al) 18 October 1983, abstract, Figures, Examples.	1-26
Y	JP 05-226211 A (FUJITSU LTD) 03 September 1993, English Abstract.	1-4
Y	JAIN, K. et al Ultrafast Deep UV Lithography with Excimer Lasers IEEE Electron Device Letters March 1982. Vol. EDL-3. No. 3. pages 53-55, especially page 54, second col., second paragraph, "5 pulses".	1-26
Y	US 4,072,524 A (KLEEBERG et al) 07 February 1978, column 2, lines 55 - column 3, lines 38, column 4, lines 25-40.	1-4
Y	US 5,250,389 A (NAKAMURA et al) 05 October 1993, column 2, lines 45-63, column 7, lines 57 - column 8, lines 54, column 10, lines 46-51, column 11, lines 36 - 47, Example 1.	1-4
Y	US 4,868090 A (KITAMURA et al) 19 September 1989, abstract.	20, 22

INTERNATIONAL SEARCH REPORT

International application No.
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07789

A. CLASSIFICATION OF SUBJECT MATTER: US CL :

430/281.1, 280.1, 300, 302, 306, 327, 945, 269, 190, 311, 285.1, 286.1; 264/401; 101/471, 463.1; 425/174.4; 347/262, 264

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

STN database service - files wpids and ca
search terms: g03f007-20/ic, g03f007-22/ic, preexpos?, pre expos?, multiple, direct writ?, digital, laser#, writ?, stereolith?, flexograph?, circuit and board, letterpress, letter press, offset, off set, interior arc, flatbed, flat bed, fluence, actinic, photo?, photohard?, photopolym?, photocur?
APS Database - file USPAT
search terms - maleate#, fumarate#, 430/281.1, 285.1, 286.1, 287.1/ccls, pre expos?, preexpos?, bump expos?, photopolym?, photoharden?, photocur?

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

- A. Referring to claims 3 and 19, methods of producing flexographic printing plates,
- B. Referring to claims 3 and 19, methods of producing letter press printing plates
- C. Referring to claims 3 and 19, methods of producing offset printing plates,
- D. Referring to claims 3 and 19, methods of producing circuit board resists,
- E. Referring to claims 3 and 19, methods of stereolithography,
- F. Referring to claim 4, methods of using (meth)acrylate based resins,
- G. Referring to claim 4, methods of using thiol/ene based resins,
- H. Referring to claim 4, methods of using vinyl ether based resins,
- I. Referring to claim 4, methods of using maleate/fumarate based resins,
- J. Referring to claim 4, methods of using cationic based resins,
- K. Referring to claim 4, methods of using naphthalene diazoquinone based resins.

The first presented species in each set of claims, ie process and apparatus with respect to flexographic printing plates being made from (meth)acrylate based resins will be searched. Claims 1-26 will be searched with this limitation.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons:

The situation involving the so - called Markush practice wherein a single claim defines alternatives (chemical or non - chemical) is governed by Rule 13.2. In this special situation, the requirement of a technical interrelationship and the same or corresponding special technical features as defined in Rule 13.2, shall be considered to be met when the alternatives are of a similar nature.

When the Markush grouping is for alternatives of chemical compounds, they shall be regarded as being of a similar nature where the following criteria are fulfilled:

- (A) all alternatives have a common property or activity, and
- (B)(1) a common structure is present, i.e., a significant structural element is shared by all of the alternatives, or
- (B)(2) in cases where the common structure cannot be the unifying criteria, all alternatives belong to a

INTERNATIONAL SEARCH REPORT

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recognized class of chemical compounds in the art to which the invention pertains.

In paragraph (B)(1), above, the words significant structural element is shared by all of the alternatives refer to cases where the compounds share a common chemical structure which occupies a large portion of their structures, or in case the compounds have in common only a small portion of their structures, the commonly shared structure constitutes a structurally distinctive portion in view of existing prior art. The structural element may be a single component or a combination of individual components linked together.

In paragraph (B)(2), above, the words recognized class of chemical compounds mean that there is an expectation from the knowledge in the art that members of the class will behave in the same way in the context of the claimed invention. In other words, each member could be substituted one for the other, with the expectation that the same intended result would be achieved.

Species A through G

The method of digitally imaging set forth by species A through G are technically separate in nature.

The process of imaging digitally via stereolithography incorporates a bath of fluid and a method controlling imaging of multiple layers or of moving imaging source in a three dimensional manner throughout the liquid bath to perform the formation of a three dimensional object. The chemical nature of the materials is different to than that needed in the printing plate art or the printed circuit art and is art recognized to be so.

The chemical and structural nature of printing plate material is quite different than circuit board resist material as well. The exposure devices for printing plates are often required to be used in circular form such as with the exterior drum device found in claim 20 and the materials to be imaged must have properties conducive to good printing properties related to each kind of plate to be formed and the manner in which ink is to be applied as well as the nature of ink interaction with the plate.

The printed circuit board processing steps with respect to imaging are quite different in requirements because the materials are used often in etching an plating processes and usually are imaged flat.

The apparatus for imaging each group are different as would be the methods of exposure and the chemical nature of the photopolymerizable material used. Thus, these alternatives fail to meet the requirement for a special technical feature which interrelates them.

Species F through K

With respect to species F through K, there is no common chemical structure shared by these groups of compounds and as such these groups fail to meet the requirement of (B)(1) above and the compositions also do not belong to a recognized class of chemical compounds in the art to which the invention pertains. Quinonediazide resins, are not ethylenically unsaturated resins and do not react via vinyl addition. (Meth)acrylate resins cure via ethylenic unsaturation and free radical polymerization. Maleate/fumarate resins contain ethylenic unsaturation in the main chain thus form crosslinks instead of polymerizing monomers forming polymers as the case with (meth)acrylate resins. Vinyl ether resins polymerize via acid or base catalyzed reactions. The cationic resins appear to refer to those cured via cationic catalyzation and that is inclusive of such systems as epoxide, melamine resins, etc.

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